PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : H01B 1/22	A1	(11) International Publication Number: WO 93/24934
		(43) International Publication Date: 9 December 1993 (09.12.93)

(21) International Application Number: PCT/GB93/01161

(22) International Filing Date: 1 June 1993 (01.06.93)

(30) Priority data:
9211500.5 30 May 1992 (30.05.92) GB

(71) Applicant *(for all designated States except US)*: FIRST CLASS SECURITIES LIMITED [-/--]; Craigmur Chambers, Road Town, Tortocla (VG).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : SLIFKIN, Michael, Arthur [GB/GB]; 25 Moorside Road, Salford M7 0PJ (GB). HAMPSHIRE, Michael, John [GB/GB]; 3 Brookfield, Upper Hopton, Mirfield WF14 8HL (GB).

(74) Agents: DOWNEY, William, Gerrard et al.; Wilson, Gunn & Ellis, 41-51 Royal Exchange, Cross Street, Manchester M2 7BD (GB).

(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: ELECTRICALLY CONDUCTIVE PASTES

(57) Abstract

Pastes for use in the production of a highly electrically conductive thick film cured by ultraviolet radiation with the primary application of screen printing interconnective patterns suitable for electronic circuits comprise a chemical which contracts on polymerisation and a metal powder pigment in the form of spherical particles. The particles advantageously comprise nickel coated with gold or silver. Metal spheres enable radiation reflected from their surfaces to penetrate the matrix to promote efficient polymerisation. The sphere size is advantageously linked to the thickness of the screen. For example, the sphere size is 4 to 15 μm for a screen thickness of 25 μm.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SK	Slovak Republic
CI	Côte d'Ivoire	KZ	Kazakhstan	SN	Senegal
CM	Cameroon	LI	Liechtenstein	SU	Soviet Union
CS	Czechoslovakia	LK	Sri Lanka	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	UA	Ukraine
DK	Denmark	MG	Madagascar	US	United States of America
ES	Spain	ML	Mali	VN	Viet Nam
FI	Finland	MN	Mongolia		

ELECTRICALLY CONDUCTIVE PASTES

The present invention relates to pastes for use in the production of a highly electrically conductive thick film cured by uv radiation with the primary application of screen printing interconnective patterns suitable for electronic circuits. The field is currently served by thermally cured pastes or inks which have a high content of silver flake. Whilst the conductivity is good being as low as 0.05m cm, the films suffer from two disadvantages. Firstly, containing such a high level of silver flake they are expensive and secondly, being thermally cured, the process is long, typically 6 to 10 minutes. This curing time makes for slow processing with the associated costs and the energy costs are also high. The current invention sets out to reduce the costs of the metal pigment or filler and to produce a uv - cured matrix which has a curing time typically of seconds rather than minutes.

Attempts to produce a uv-cured ink with flake shaped pigments have not met with success. It is believed that the geometrical stacking of plates prevents the penetration of uv radiation between the flakes and hence satisfactory polymerisation is not achieved.

According to the present invention there is provided

a paste comprising at least one chemical which contracts on polymerisation together with metal powder pigment substantially of a spherical geometry with an outer surface of a metal which either does not oxidise or produces a very thin stable oxide.

Advantageously, the metal of the pigment is ferromagnetic, preferably nickel powder.

The size of the spheres advantageously matches the thickness and definition requirements of the screen printing process. For 25μm thick films a particle size distribution from 4μm to 15μm has been found to be successful.

The provision of a metal surface which, when oxidised, produces a very thin stable oxide enables electrons to tunnel through the dielectric layer between the metal spheres. Coatings which do not oxidise, the noble metals such as gold (Au) for example, are, of course, very suitable. Silver (Ag) produces a thin stable oxide and is most suitable. Copper (Cu) on the other hand does not have a suitable oxide.

Copper spheres are attractive on a resistivity and cost basis although adhesion of other metal coatings may in some cases be difficult. On the other hand adhesion

of silver (Ag) to nickel (Ni) is good and this has been shown to be a successful combination, namely that of silver (Ag) coated nickel (Ni) spheres.

The use of nickel (Ni) spheres in conductive thick film sheets has a further major advantage, in that the ferromagnetic nature of Ni reduces the wavelength of any electromagnetic waves propagating through the film. The film, therefore, has a smaller skin depth and hence attenuates an electromagnetic wave more effectively. The attenuation coefficient, a, of an electromagnetic wave of angular frequency, w, through a film of resistivity, p, and permeability, μ, is given by

$$a = \sqrt{(w\mu/p)}$$

As the relative permeability of pure Ni is about 250, then a film largely composed of Ni spheres will be expected to attenuate up to about 15 times more effectively than a non-ferromagnetic film of the same resistivity.

The pigment spheres are advantageously blended with a binding polymer and a photointiator to promote the uv curing of the polymer. Further, a diluent is preferably added to generate the appropriate rheology suitable to screen printing. A viscosity in the range of 5 to 150 poise is appropriate. Finally, the formulation benefits from the addition of small amounts of three further

chemicals to improve adhesion, abrasion resistance and to minimise bubble formation.

The requirements of the basic polymer is important in that for good results the material must contract on curing, such that the pigment sphere are compressed together in the final film so promoting good electrical contact from one sphere to the next. In this respect a satisfactory polymer has been found to be urethane acrylate.

In order that the invention may be more clearly understood, one embodiment will now be described by way of example.

The embodiment comprises the following formulation (as a percentage by weight)

Silver coated nickel spheres 4 to 15µm	44.15g
Urethane Acrylate	1.25g
Acrylic monomer viscosity modifier	3.35g
Photoinitiator	0.8g
Additives	0.5g

This produces a film with a resistivity of 0.3mΩcm, after curing for a few seconds in uv radiation from a medium pressure Hg lamp with a power of 125W at a

distance of about 20cms from the sample. The major uv emission from the medium power lamp is at a wavelength of 365nm.

Typical chemicals in the formulation could be:-

Photomer 6140 - Aliphatic Polyester Urethane Acrylate dissolved in Tripropylene glycol diacrylate.

* Viscosity modifier 4237 - Tripropylene glycol diacrylate
both from Harcros Chemicals UK Ltd.

* Photoinitiator 4265 combination of Acrylic Keytone with Lucirin TPO, available from Ciba Geigy, Basle, Switzerland.

* The additives. Antibubble - blend of surface active agents in solution including Lecithin and polyvinyl alcohol, Lanco flow - Acrylic copolymer and Lanco-Wax TS1778 - modified micronised PTFE wax are available from Capricorn Chemicals Ltd.

These are used respectively to prevent bubble formation, to increase adhesion and to improve the abrasion resistance.

A post cure treatment is found to significantly reduce the resistivity. It is known that uv radiation promotes polymerisation to about 95%. Further polymerisation can be achieved by a number of methods such as:-

* Heat treatment
* Infra Red heating
* RF heating
* Electron beam irradiation
* Higher energy uv radiation from a low pressure Hg lamp with a major emission at 254nm.

Baking the films in an oven for 6 hours at 100°C reduces the resistivity from 0.3mΩcm to 0.05mΩcm.

The use of metal spheres overcomes the problem of uv radiation penetration experienced with the prior art flakes by enabling the radiation reflected from their surfaces to penetrate the matrix and promote efficient polymerisation.

It will be appreciated that the above embodiment has been described by way of example only and that many variations are possible without departing from the scope of the invention.

CLAIMS

1. A paste comprising at least one chemical which contracts on polymerisation together with metal powder pigment substantially of a spherical geometry with an outer surface of a metal which either does not oxidise or produces a very thin stable oxide.

2. A paste as claimed in claim 1, in which the metal powder pigment is fluromagnetic.

3. A paste as claimed in claim 1 or 2, in which the metal powder pigment is nickel.

4. A paste as claimed in any of claims 1 to 3, in which the particle size of the metal powder pigment is linked to the thickness of the screen printing process in which the paste is to be used.

5. A paste as claimed in claim 4, in which the particle size lies in the range 4μm to 15μm for a screen thickness of 25μm.

6. A paste as claimed in any preceding claim, in which the surface of the metal is a coating of a noble metal.

7. A paste as claimed in claim 6, in which the noble

metal is gold.

8. A paste as claimed in claim 6, in which the noble metal is silver.

9. A paste as claimed in any preceding claim in which the metal powder pigment is blended with a binding polymer and a photoinitiator to promote the curing of the polymer.

10. A paste as claimed in any preceding claim, in which a diluent is added having a viscosity in the range of 5 to 150 poise.

11. A paste as claimed in any preceding claim including chemicals to improve adhesion, abrasion resistance and to minimise bubble formation.

12. A paste formulated in accordance with the example described in the specification.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 93/01161

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: H01B 1/22
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A2, 0174776 (MINNESOTA MINING AND MANUFACTURING COMPANY), 19 March 1986 (19.03.86), page 3, line 9 - page 4, line 8; page 6, line 18 - page 7, line 9	1,2,3,6,7,8, 9,11
Y		4,5,10,12
X	EP, A1, 0343836 (POTTERS INDUSTRIES, INC.), 29 November 1989 (29.11.89), column 1, line 26 - column 2, line 23; column 2, line 41 - line 52; column 5, line 7 - line 43, column 6, line 10 - line 18; column 6, line 40 - column 7, line 27	1,2,3,6,7,8
Y	column 5, line 44 - column 6, line 1; column 6, line 10 - line 33	4,5,9-12

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 Sept 1993	20. 10. 93

Name and mailing address of the International Searching Authority	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Nils Engnell

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 93/01161

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A1, 0234347 (INTERNATIONAL BUSINESS MACHINES CORPORATION), 2 Sept 1987 (02.09.87), page 2, line 17 - page 1, line 26; page 3, line 38 - line 41; page 4, line 4 - line 19, page 5, line 4 - line 24	1,6,7,8,9
Y		10
A		2,3,4,5,11, 12
X	EP, A2, 0291064 (E.I. DU PONT DE NEMOURS AND COMPANY), 17 November 1988 (17.11.88)	1,6,7,8
A		2-5,9-12
Y	EP, A1, 0081323 (JOHNSON MATTHEY PUBLIC LIMITED COMPANY), 15 June 1983 (15.06.83), page 1, line 1 - page 4, line 12; page 9, line 9 - line 19; page 11, line 2 - line 18	9-11
A		1-8,12
X	Derwent's abstract, No 87-275700/39, week 8739, ABSTRACT OF SU, A1, 1098-441 (KHIMCHENKO YU I), 7 March 1987 (07.03.87)	1,2,3
A		4-12
A	US, A, 4732702 (MITSUO YAMAZAKI ET AL), 22 March 1988 (22.03.88)	1-12

S/ 5620

INTERNATIONAL SEARCH REPORT

Information on patent family members

26/08/93

International application No.
PCT/GB 93/01161

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0174776	19/03/86	AU-A- 4508585	13/03/86
		JP-A- 61066309	05/04/86
		US-A- 4546037	08/10/85
EP-A1- 0343836	29/11/89	AU-B- 614122	22/08/91
		AU-A- 3390889	30/11/89
		JP-A- 1320704	26/12/89
		US-A- 4857233	15/08/89
EP-A1- 0234347	02/09/87	JP-A- 62199611	03/09/87
		US-A- 4780371	25/10/88
		US-A- 4859268	22/08/89
EP-A2- 0291064	17/11/88	DE-A- 3880884	17/06/93
		JP-A- 63301274	08/12/88
EP-A1- 0081323	15/06/83	CA-A- 1181580	29/01/85
		GB-A- 2111072	29/06/83
		JP-A- 58104971	22/06/83
US-A- 4732702	22/03/88	GB-A,B- 2186577	19/08/87
		JP-A- 62275180	30/11/87
		NL-A- 8700189	01/09/87